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Dedicated to the 115th anniversary of B.A. Arbuzov's birth

Synthesis and Complexing Properties of *p*-Toluensulfonylamido and Phosphorylamido Derivatives of Second-Generation Hyperbranched Polyester

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Abstract—Hyperbranched polyesters containing terminal *p*-toluenesulfonylamido and diethoxyphosphorylamido groups have been synthesized, and their complexes with copper(II) and cobalt(II) ions have been prepared. The thermal stability of the ligands and their metal complexes has been studied by differential scanning calorimetry.

Keywords: hyperbranched polyester, copper complexes, thermal stability

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Nontoxic nanosized hyperbranched polyesters possess a broad spectrum of biological properties and are used as drug delivery vehicles and polydentate macroligands. Hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid and their derivatives have found application in various fields such as modification of polymeric materials (paint-and-lacquer coatings, polymeric nanocomposites), manufacture of electro-optical materials, extraction of metals from aqueous medium, and pharmacology (as nanocontainers) [1–13]. Amino derivatives of hyperbranched polyesters form supramolecular systems with DNA and RNA molecules and exhibit high complexing power toward 3*d* metal ions [5, 14–17]. Introduction of phosphorus and sulfur atoms into terminal positions of polyesters endows them with thermal stability and enhances their pharmacophoric properties [18–20]. Hyperbranched polyesters with terminal amino, tosylateamido, or phosphorylamido groups have not been reported.

The present study was aimed at synthesizing new hyperbranched polyesters possessing polyfunctional terminal N,P- and N,S-containing groups, determining their structure, and evaluating their complexing ability. A second-generation hyperbranched polyester polyol containing 16 terminal hydroxy groups was selected as initial structure for functionalization. Its reaction with acryloyl chloride according to the procedure described in [17] gave polyacrylate **1**. The ^{1}H NMR data showed that the esterification involved 10 most sterically accessible hydroxy groups. Hyperbranched polyesters with terminal *p*-toluenesulfonylamido and diethoxyphosphorylamido groups were synthesized in two steps (Scheme 1). In the first step, 4-toluenesulfonyl chloride and diethyl chlorophosphate were reacted with ethylenediamine to obtain *N*-(2-aminoethyl)-4-methylbenzenesulfonamide (**2**) and diethyl *N*-(2-aminoethyl)phosphoramidate (**3**), respectively. The second step was nucleophilic addition of **2** or **3** to the terminal C=C bonds of **1**, which afforded target compounds **4** and **5**.

Unlike the initial second-generation hyperbranched polyester polyol [21], the IR spectrum of **4** showed increased intensity of the broadened O–H stretching band in the region 3600–3150 cm^{-1} due to a contribution of N–H stretching vibrations. The ester carbonyl band of **4** was observed at 1733 cm^{-1}. The IR spectrum of **4** lacked C=C stretching bands (1635, 1618 cm^{-1}) and bands at 1408, 1296 and 983, 808 cm^{-1} typical of in-plane and out-of-plane bending vibrations of C–H bonds in the =CH$_2$ group. These findings